

PATENT SPECIFICATION

(11) 1236949

NO DRAWINGS

(21) Application No. 47795/68 (22) Filed 9 Oct. 1968

(23) Complete Specification filed 30 Sept. 1969

(45) Complete Specification published 23 June 1971

(51) International Classification C 08 g 17/015

(52) Index at acceptance

C3R 3D13 3D2E 3N1 3P4

C1A N30

C2C 3A10A1 3A10A5A1 3A13A1A1 3A13A1C

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(54) CATALYTIC PROCESS FOR MAKING POLYESTERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of polyesters wherein the polycondensation stage is catalysed by the joint presence of a pentavalent antimony compound and a tin compound.

According to the present invention we provide a process for the preparation of a high molecular weight linear polyester by the polycondensation of a bis(ω -hydroxyalkyl) terephthalate using as polycondensation catalysts both a compound of antimony in the pentavalent state which is soluble in the reaction mixture and a compound of tin which is soluble in the reaction mixture.

The bis (ω -hydroxyalkyl) terephthalate employed in the process of our invention may be prepared by any known method. In some modes of preparation of the bis (ω -hydroxyalkyl) terephthalate there is a somewhat arbitrary distinction between the stage of preparation of the intermediate product and the start of the polycondensation stage and the addition of the antimony compound and/or the addition of the tin compound may be delayed until after some degree of polycondensation has been effected.

In the case wherein the preparation of bis (ω -hydroxyalkyl) terephthalate involves an ester-interchange reaction, a suitable ester-interchange catalyst will normally be used in which case a phosphorus compound must be added at the end of the ester-interchange reaction in such an amount as to inhibit any adverse effect of the ester-interchange catalyst during the polycondensation stage. In that case the phosphorus compound must be of such type and in such quantity that no adverse effect is produced on either the antimony or the tin catalyst. For example, the insolubilisa-

tion of the antimony or the tin must be avoided. Preferably the phosphorus compound used should be an acid of phosphorus or an ester of such acid. Of particular value are phosphoric acid or an inorganic or organic phosphate. Examples of phosphorus compounds which we have found suitable are phosphorous acid, phosphoric acid, trimethyl phosphite, triphenyl phosphite, triphenyl phosphate, sodium dihydrogen phosphate, tris(dipropylene glycol) phosphonate, hydrogenated 4:4' - isopropylidene diphenol phosphite and tri(nonylphenyl) phosphite.

The quantity of antimony compound used as catalyst should be such as to correspond to at least 5 parts per million of antimony metal based on the bis(ω -hydroxyalkyl) terephthalate. The quantity of tin compound used as joint catalyst should be such as to correspond to at least 5 parts per million of tin metal based on the bis(ω -hydroxyalkyl) terephthalate. The relative quantities of the antimony and the tin compound should be such as to correspond to at least 0.5 atom of antimony to one atom of tin and may be as high as 30 atoms of antimony to one atom of tin. Advantageously the relative quantities should be such as to correspond to at least 1 atom of antimony to one atom of tin but not to be in excess of 10 atoms of antimony to one atom of tin. Particularly good results have been obtained by us when the relative quantities of the antimony and tin compounds were such as to correspond to from 1.3 to 5 atoms of antimony to one atom of tin.

Although the benefits of our invention are obtained when the antimony and tin compounds are each added at the same time and at any stage from the start of the preparation of the bis(ω -hydroxyalkyl) terephthalate, where appropriate this may be after some degree of polycondensation has been effected; either the antimony or the tin compound may be added first followed by the second compound. However, in such case it is preferable to add the antimony compound first.

In the term polyester we also include co-

polyester, the copolyester being prepared by modification of the process hereinbefore described according to known principles. The process of our invention is of particular utility in the manufacture of polyesters or copolyesters for the manufacture of fibres. For this application the copolyester molecule should preferably consist of at least 80% of units of a single alkylene terephthalate; the remaining structural units may, for example, be based on a second dicarboxylic acid, for example adipic or isophthalic acid, or a second glycol. Advantageously the alkylene terephthalate units are ethylene terephthalate.

Suitable antimony compounds for use in the process of our invention are, for example, antimonious acid, antimony pentaglycoloxide, antimony pentoxide including hydrates of antimony pentoxide and potassium antimonate.

Suitable tin compounds for use in the process of our invention are, for example, stannous formate, stannous acetate, stannous octanoate, stannous oxalate, stannous chloride, stannic chloride, dioctyl thio tin, that is $(C_8H_{17})_2SnS$, dibutyl tin oxide, dibutyl tin acetate, dibutyl tin laurate, dibutyl tin maleate and tetrabutyl tin.

An advantage of the process of our invention is that by the use of it polyesters may be prepared using a short reaction cycle time and having visual appearance superior to that obtainable in the same reaction cycle time using pentavalent antimony compound alone, tin compound alone or trivalent antimony compound conjointly with tin compound.

Provided that it meets the above described requirements, a single compound may be used as the polycondensation catalyst, the single compound being both a compound of pentavalent antimony and a compound of tin.

A suitable temperature at which to carry out the polycondensation stage is between 250 and 350°C.

A fibre-forming molecular weight is above about 8,000, which corresponds to Viscosity Ratio 1.33 as measured at 1% in solution in orthochlorophenol at 25°C.

Other additives commonly present in polyesters may be added in the amount commonly used. Examples of such additives are phosphorus compounds, delustrants, optical whiteners and coloured materials.

Preferably the quantity of antimony compound present in the polycondensation reaction should not exceed that corresponding to 1,000 parts per million of antimony metal based on the bis (ω -hydroxylalkyl) terephthalate and the quantity of tin compound present in the polycondensation reaction should not exceed that corresponding to 500 parts per million of tin metal based on the bis(ω -hydroxylalkyl) terephthalate.

In order that the nature of the process of our invention should be the more clearly understood, we give hereinafter Examples

3—7, 12—20, 22—26, 36—40, and 46—94, Examples 1, 2, 8, 9, 10, 11, 21, 27—35 and 31—45 are for comparative purposes. In all examples all parts are by weight.

A series of experiments was carried out using the following general method of procedure:

Dimethyl terephthalate (1552 parts) and ethylene glycol (1,235 parts) were reacted together under ester-interchange conditions in the presence of an ester-interchange catalyst. The reaction was carried out under reflux with final temperature 215—220°C, completion of reaction being judged by the evolution of approximately the theoretical quantity of methanol. The particular phosphorus compound used (if any) was then added and 5 minutes later titanium dioxide delustrant (7.76 parts) was added in the form of a slurry in ethylene glycol at 20% w/w concentration (except where otherwise stated). This was followed by the tin and antimony compounds, usually in that order except where indicated otherwise. These compounds were either pre-dissolved or slurried with ethylene glycol at 5.0% w/v concentration before addition. The tin and antimony compounds were added within 5 minutes of each other except where indicated otherwise. The resultant product was then transferred to a stainless steel autoclave and the temperature of the reactants raised to 290°C during 30 minutes, vacuum being applied from the time of attaining 235°C so that the pressure was less than 1 mm. of mercury 30 minutes after the start of application of vacuum. In cases where late addition is indicated, the addition was made when the pressure had reached 1 mm. of mercury. The polycondensation stage was judged to be complete when the power required to drive the agitator reached the value previously ascertained to correspond to the required molecular weight. The time taken for the polycondensation was counted from the earliest attainment of a temperature of the reactants of 285°C simultaneously with pressure falling below 1 mm. of mercury.

Intrinsic Viscosity (I.V.) was measured at 8% concentration (w/w) in orthochlorophenol at 25°C.

A superior visual appearance of polyester leads to superior fibre appearance. A measure of the superior visual appearance of the polyester is a high value for L—Y accompanied by a high value of L. L and Y refer to Luminance and Yellowness determined using a "Colormaster" differential colorimeter manufactured by the Manufacturers Engineering Equipment Corporation.

The antimonious acid, used in some of the examples, had the composition $Sb_2O_3 \cdot xH_2O$. This was taken into account in calculation of parts per million (ppm) given in column 6 of Table 1 and column 7 of Table 2 and column 8 in Table 3, the parts per million being based

in the case of the ester-interchange route on the weight of dimethyl terephthalate charged and in the case of the esterification of terephthalic acid, on the weight of terephthalic acid.

5 In the Series A examples the phosphorus compound charged was $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ used at 0.025% based on dimethyl terephthalate. The polycondensation catalysts were separately predissolved in glycol before charging.

10 In Series B examples the phosphorus compound charged was triphenyl phosphite used at 0.6% based on dimethyl terephthalate. The catalysts were predissolved in ethylene glycol and the solutions mixed before charging.

15 In series C examples the phosphorus compound charged was triphenyl phosphite used at 0.06% based on dimethyl terephthalate. The catalysts were each dissolved in ethylene glycol and the solutions mixed before charging.

20 In Series D examples the phosphorus compound charged was triphenyl phosphite used at 0.06% based on dimethyl terephthalate, except for example 30 wherein



25 was charged at 0.023% based on dimethyl terephthalate. The catalysts were each predissolved separately in ethylene glycol before charging.

30 In Series E examples the phosphorus compound charged was $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ used at 0.025% based on dimethyl terephthalate. The catalysts were each predissolved separately in glycol before charging.

35 In Series F examples the phosphorus compound charged was $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ used at

0.025% based on dimethyl terephthalate. In these examples either a tin or antimony compound was used as polycondensation catalyst alone and this was predissolved in glycol before charging.

40 In Series G the catalysts were predissolved separately in glycol before addition in all examples with the exception of Example 63 in which the stannic chloride and potassium antimonate were heated together in glycol until a clear solution was obtained.

45 In Series J, K, L, M, N, O, P and Q the catalysts were separately predissolved in glycol before charging.

50 In Example 82, the triphenyl phosphite was added after the catalysts, as opposed to the other examples.

55 In Example 88 no titanium dioxide de-lustrant was charged. In view of this it was not possible to carry out the measurement of Luminance and Yellowness since these would not be meaningful. The polyester produced was, however, clear and colourless.

60 In Example 89 titanium dioxide was charged in the amount to yield a polyester containing 2.0% of titanium dioxide.

65 In Examples 83, 84, 85 and 86, zinc acetate (0.12% based on dimethyl terephthalate) was used as ester-interchange catalyst. In Example 87, calcium acetate (0.07% based on dimethyl terephthalate) was used as ester-interchange catalyst. In all other examples involving ester-interchange, manganese acetate (0.025% based on dimethyl terephthalate) was used as ester-interchange catalyst. In each case the percentage is as the anhydrous salt.

TABLE I

| Series | Example No. | Sn Compound | Sn ppm. | Sb Compound | Sb ppm | Sb/Sn atomic ratio | Polymerisation time (min.) | I.V. | L | Y | L-Y |
|--------|-------------|-----------------------|---------|-------------|--------|--------------------|----------------------------|------|----|----|-----|
| A | 1 | SnOx | 115 | None | Nil | 0 | 85 | .662 | 74 | 41 | 33 |
| | 2 | " | 102 | AA | 50 | .48 | 85 | .659 | 75 | 35 | 40 |
| | 3 | " | 92 | " | 91 | .97 | 62 | .650 | 77 | 31 | 46 |
| | 4 | " | 86 | " | 117 | 1.33 | 67 | .620 | 81 | 20 | 61 |
| | 5 | " | 57 | " | 254 | 4.35 | 76 | .629 | 79 | 19 | 60 |
| | 6 | " | 48 | " | 292 | 5.9 | 71 | .671 | 75 | 13 | 62 |
| | 7 | " | 29 | " | 351 | 11.8 | 65 | .665 | 70 | 12 | 58 |
| | 8 | " | 13 | " | 409 | 37.6 | 85 | .721 | 51 | 6 | 45 |
| | 9 | None | Nil | " | 468 | ∞ | 55 | .657 | 66 | 14 | 52 |
| B | 10 | Sn(Form) ₂ | 213 | None | Nil | 0 | 40 | .655 | 69 | 58 | 11 |
| | 11 | " | 176 | AA | 87 | .48 | 31 | .662 | 74 | 43 | 31 |
| | 12 | " | 150 | " | 148 | .97 | 34 | .667 | 75 | 38 | 37 |
| | 13 | " | 138 | " | 177 | 1.25 | 38 | .680 | 76 | 36 | 40 |
| | 14 | " | 116 | " | 229 | 1.93 | 43 | .696 | 78 | 27 | 51 |
| | 15 | " | 94 | " | 280 | 2.9 | 47 | .640 | 82 | 21 | 62 |
| | 16 | " | 75 | " | 326 | 4.25 | 55 | .706 | 79 | 15 | 64 |
| | 17 | " | 68 | " | 335 | 4.8 | 46 | .654 | 80 | 15 | 65 |
| | 18 | " | 61 | " | 424 | 6.8 | 42 | .680 | 74 | 14 | 60 |
| | 19 | " | 41 | " | 406 | 9.7 | 47 | .677 | 73 | 13 | 60 |
| | 20 | " | 16 | " | 467 | 28.4 | 51 | .713 | 70 | 12 | 58 |
| | 21 | None | Nil | " | 504 | ∞ | 39 | .697 | 68 | 18 | 50 |

TABLE I (continued)

| Series | Example No. | Sn Compound | Sn ppm. | Sb Compound | Sb ppm | Sb/Sn atomic ratio | Polymerisation time (min.) | I.V. | L | Y | L-Y |
|--------|-------------|-------------------------------------|---------|--------------------------------|--------|--------------------|----------------------------|------|----|------|------|
| C | 22 | DBTA | 153 | AA | 159 | 1.01 | 38 | .673 | 77 | 30 | 47 |
| | 23 | " | 116 | " | 236 | 2.0 | 50 | .675 | 79 | 22 | 57 |
| | 24 | " | 87 | " | 236 | 3.7 | 43 | .681 | 82 | 16 | 66 |
| | 25 | " | 51 | " | 371 | 7.3 | 47 | .668 | 76 | 15 | 61 |
| | 26 | " | 44 | " | 438 | 9.7 | 51 | .670 | 73 | 16 | 57 |
| | 27 | SnAc ₂ | 112 | None | Nil | 0 | 50 | .689 | 73 | 40 | 33 |
| D | 28 | " | 93 | Sb ₂ O ₃ | 210 | 2.2 | 50 | .688 | 74 | 30 | 44 |
| | 29 | " | 74 | " | 285 | 3.75 | 55 | .605 | 75 | 29.5 | 45.5 |
| | 30 | SnOX | 57 | " | 252 | 4.3 | 61 | .641 | 77 | 27 | 50 |
| | 31 | SnAc ₂ | 70 | " | 378 | 5.3 | 34 | .680 | 78 | 27 | 51 |
| | 32 | SnCl ₄ 5H ₂ O | 74 | " | 378 | 4.99 | 40 | .585 | 77 | 29 | 48 |
| | 33 | SnAc ₂ | 42 | " | 462 | 10.7 | 45 | .643 | 71 | 26 | 45 |
| | 34 | " | 23 | " | 504 | 21.3 | 59 | .684 | 67 | 14 | 53 |
| | 35 | None | Nil | " | 504 | ∞ | 63 | .696 | 58 | 2 | 56 |
| | 36 | SnOx | 35 | AA | 97 | 2.7 | 89 | .674 | 80 | 22 | 58 |
| | 37 | " | 54 | " | 156 | 2.8 | 74 | .596 | 81 | 20 | 61 |
| E | 38 | " | 69 | " | 195 | 2.8 | 65 | .660 | 82 | 19 | 63 |
| | 39 | " | 98 | " | 280 | 2.8 | 63 | .661 | 80 | 19 | 61 |
| | 40 | " | 115 | " | 325 | 2.8 | 49 | .696 | 80 | 21 | 59 |
| | 41 | SnOx | 58 | None | Nil | 0 | 102 | .648 | 79 | 28 | 51 |
| F | 42 | " | 115 | " | " | 0 | 85 | .662 | 74 | 41 | 33 |
| | 43 | None | Nil | AA | 234 | ∞ | 80 | .676 | 69 | 10 | 59 |
| | 44 | " | " | " | 325 | ∞ | 75 | .708 | 68 | 12 | 56 |
| | 45 | " | " | " | 468 | ∞ | 55 | .567 | 66 | 14 | 52 |

TABLE 2

| Series | Example No. | P Compound | Sn Compound | Sb Compound | Sn ppm | Sb ppm | Sb/Sn atomic ratio | Polymerisation time (min.) | I.V. | L | Y | L-Y |
|--------|-------------|------------------------------|-----------------------|-------------|--------|--------|--------------------|----------------------------|------|------|----|------|
| G | 46 | .018 H_3PO_4 | SnOx | AA | 58 | 234 | 3.9 | 61 | .601 | 78 | 17 | 61 |
| | 47 | .023 $NaH_2PO_4 \cdot 5H_2O$ | " | " | 58 | 234 | 3.9 | 65 | .723 | 79 | 19 | 60 |
| | 48 | " | $SnCl_4 \cdot 2H_2O$ | " | 51 | 234 | 4.5 | 72 | .674 | 81 | 16 | 65 |
| | 49 | " | $SnCl_4 \cdot 5H_2O$ | " | 58 | 234 | 3.9 | 64 | .661 | 80 | 15 | 65 |
| | 50 | .06 Ph_3PO_4 | SnOx | " | 69 | 195 | 2.8 | 55 | .670 | 82 | 16 | 66 |
| | 51 | .015 PA | $SnAc_2 \cdot H_2O$ | APGO | 65 | 250 | 3.75 | 77 | .685 | 81 | 15 | 66 |
| | 52 | " | SnOx | AA | 69 | 195 | 2.8 | 70 | .675 | 80 | 16 | 64 |
| | 53 | " | $SnCl_4 \cdot 5H_2O$ | " | 68 | 195 | 2.8 | 66 | .690 | 80 | 15 | 65 |
| | 54 | " | $(C_6H_{17})_3SnS$ | " | 63 | 195 | 3.0 | 80 | .630 | 79 | 22 | 57 |
| | 55 | .06 TPP | $SnCl_4 \cdot 2H_2O$ | " | 75 | 326 | 4.2 | 60 | .660 | 79 | 14 | 65 |
| | 56 | " | $SnCl_4 \cdot 5H_2O$ | " | 75 | 326 | 4.2 | 42 | .655 | 81 | 16 | 65 |
| | 57 | " | $Sn(oct.)_2$ | " | 73 | 326 | 4.35 | 48 | .679 | 80.5 | 15 | 66.5 |
| | 58 | " | DBTO | " | 81 | 326 | 3.9 | 51 | .669 | 82 | 17 | 65 |
| | 59 | " | DBTA | " | 87 | 326 | 3.7 | 43 | .681 | 82 | 20 | 62 |
| | 60 | " | DBTL | " | 69 | 326 | 4.6 | 49 | .677 | 81 | 19 | 62 |
| | 61 | " | DBTM | " | 69 | 326 | 4.7 | 47 | .669 | 81 | 22 | 59 |
| | 62 | " | $SnBu_4$ | " | 70 | 326 | 4.5 | 54 | .664 | 77 | 15 | 62 |
| | 63 | " | $SnCl_4 \cdot 5H_2O$ | $KSb(OH)_6$ | 70 | 325 | 4.5 | 55 | .660 | 77 | 13 | 64 |
| | 64 | .024 TMP | $SnAc_3 \cdot H_2O$ | AA | 70 | 342 | 4.75 | 64 | .666 | 79 | 18 | 61 |
| | 65 | .09 TNPP | " | " | 70 | 336 | 4.7 | 45 | .650 | 81 | 17 | 64 |
| | 66 | .09 HPDIPP | " | " | 70 | 336 | 4.7 | 56 | .700 | 79 | 13 | 66 |
| H | 67 | .06 TPP | $SnAc_3 \cdot H_2O^*$ | AA* | 70 | 336 | 4.7 | 80 | .707 | 78 | 17 | 61 |
| | 68 | " | " | " | 70 | 336 | 4.7 | 50 | .649 | 80 | 16 | 64 |
| | 69 | " | " | " | 70 | 336 | 4.7 | 48 | .660 | 79 | 16 | 63 |

TABLE 2 —Continued

[illegible]

EXAMPLES 90-93

Terephthalic acid (1,328 parts) and ethylene glycol (775 parts in the case of Example 90 and 745 parts in the case of Examples 91, 92 and 93) were heated together (in the presence of sodium hydroxide where indicated) to a temperature of 230°C. and reacted with gradually rising temperature to final temperature 260°C. with periodical venting off of the water vapour formed by the reaction in order to maintain a total pressure of 40 pounds per square inch gauge. The total reaction time was 120 minutes. The temperature of the reaction mixture was then raised to 290°C. and the reaction continued under a pressure of 0.2 mm. of mercury. The degree of polycondensation was interpolated from the power re-

quired to drive the agitator and was judged to have reached the desired stage. The time for polycondensation is calculated from the point at which the pressure fell below 1 m.m. of mercury. In the Examples wherein a phosphorus compound is present, this was added at the end of the initial esterification before the pressure was reduced for the polycondensation stage.

The data for these Examples are given in Table 3 wherein the quantity of sodium hydroxide and of the phosphorus compound are expressed as a percentage based on the terephthalic acid charged. The parts per million of tin and of antimony are each expressed in the form of the metal referred to the weight of terephthalic acid charged.

TABLE 3

| Series | Example No. | NaOH % | P % Compound | Sn Compound | Sb Compound | Sn ppm | Sb ppm | Sb/Sn atomic ratio | Polymerisation time (min.) | I.V. | L | Y | L-Y |
|--------|-------------|--------|--------------------------------------|-------------------------------------|-------------|--------|--------|--------------------|----------------------------|------|------|----|------|
| Q | 90 | Nil | Nil | SnAc ₂ .H ₂ O | AA | 82 | 395 | 4.7 | 58 | .665 | 79 | 22 | 56 |
| | 91 | Nil | .0058 H ₃ PO ₄ | SnOx | " | 68 | 273 | 3.9 | 55 | .674 | 78 | 22 | 56 |
| | 92 | .0058 | .015 PA | SnAc ₂ .H ₂ O | " | 82 | 356 | 4.25 | 75 | .714 | 76.5 | 19 | 57.5 |
| | 93 | " | .044 TPP | " | " | 82 | 391 | 4.7 | 88 | .713 | 73 | 18 | 55 |

NOTES ON TABLES

- (1) All recipe figures are percentages by weight on dimethyl terephthalate or terephthalic acid charged.
- (2) HIPDIPP = hydrogenated 4:4'-isopropylidene diphenol phosphite.
- (3) AA = Antimonic acid.
- (4) Ac = Acetate radical.
- (5) APGO = Antimony pentaglycoloxide.
- (6) Bu = Butyl.
- (7) DBTA = Dibutyl tin diacetate.
- (8) DBTL = Dibutyl tin dilaurate.
- (9) DBTM = Dibutyl tin maleate.
- (10) DBTO = Dibutyl tin oxide.
- (11) Form. = Formate radical
- (12) l = Late (in connection with late addition).
- (13) Oct. = Octanoate radical.
- (14) Ox. = Oxalate radical.
- (15) PA = Phosphorous acid.
- (16) P/C = Polycondensation.
- (17) Ph = Phenyl radical.
- (18) TMP = Trimethyl phosphite.
- (19) TNPP = tri(nonylphenyl) phosphite.
- (20) Ph_3PO_4 = Triphenyl phosphate.
- (21) TPP = Triphenyl phosphite

EXAMPLE 94

This demonstrates the preparation of a copolyester according to the process of our invention.

Dimethyl terephthalate (1,241 parts) and ethylene glycol (1,235 parts) were reacted together under ester-interchange conditions in the presence of manganese acetate tetrahydrate (0.551 parts) as catalyst. The reaction was carried out under reflux with final temperature 215–220°C., completion of reaction being judged by the evolution of approximately the theoretical quantity of methanol. After completion of ester-interchange, isophthalic acid (264 parts) was added and the temperature raised to 245°C. and reaction continued under a total pressure of 40 pounds per square inch gauge, the pressure being maintained by periodic venting off the water vapour pro-

duced by reaction. Reaction was complete in 30 minutes. The pressure was then released over 10 minutes. To the reaction mixture were charged triphenyl phosphite, tin acetate ($\text{SnAc}_2 \cdot \text{H}_2\text{O}$) and antimonic acid, the quantity of each of the three being equivalent to that charged in Example 67, that is based on the weight of dimethyl isophthalate equivalent to the isophthalic acid charged the quantities were 0.06% of triphenyl phosphite, 70 parts per million of Sn and 336 parts per million of Sb. The resultant product was then transferred to a stainless steel autoclave and polycondensation carried out as described hereinbefore for the ester-interchange method.

The polymerisation time was 80 minutes giving a copolyester of Intrinsic Viscosity of 0.67, a Luminance of 72.5 and a Yellowness of 20. The ratio of Sb/Sn used was 4.7;

Preparation of Antimony Pentaglycoloxide

Antimonic acid, with the approximate formula $\text{Sb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ or $\text{HSb}(\text{OH})_6$, was prepared from potassium antimonate $\text{KSb}(\text{OH})_6$.

- 5 The potassium antimonate (50 g.) was dissolved in 100 parts of water. To the solution was added 5M nitric acid (50 parts), slowly and with good agitation. The white precipitate formed was filtered off and washed free from nitric acid with water and dried in air at 25°C. until the free moisture content (measured by drying *in vacuo* at 25°C. for 24 hours) was less than 8%.

- 10 Within 48 hours of preparation, the antimonic acid (1 part) was dissolved by boiling under reflux in ethylene glycol (4 parts) for not more than one hour; water vapour was allowed to escape freely from the system during the heating up and refluxing. The solution was filtered at a little above 100°C. if necessary, and allowed to cool to 25°. The precipitation of solid white antimony pentaglycoloxide was then assisted by the addition of acetone equal in volume to twice that of the

solution. After allowing to stand for 6 hours, the solid precipitate was filtered under suction and dried *in vacuo* at 25° for 24 hours.

The product contained (50±5)% $\text{Sb}(\text{V})$ (theoretical for $\text{Sb}_2(\text{OCH}_2\text{CH}_2\text{O})_5 = 44.9\%$). The $\text{Sb}(\text{III})$ content was below 0.5%.

Preparation of Tin Acetate

30 g. black stannous oxide containing not less than 70% SnO , the remainder being substantially SnO_2 , were added to 1,000 ml glacial acetic acid and the mixture was heated to the boiling point and boiled under reflux for 1 hour, water vapour and a little acetic acid vapour being allowed to escape. The hot liquor was then filtered on a preheated filter to remove solid material, and allowed to cool to 25°C. A creamy-white voluminous precipitate of tin acetate was formed. This was freed from acetic acid by filtration under suction and drying for 48 hours at 25°C *in vacuo*.

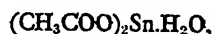
The dried solid tin acetate was analysed as shown in Table 4 (percentage composition).

TABLE 4

| | Material prepared as described | $\text{Sn}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ theoretical |
|-----------------------------|-----------------------------------|---|
| Sn | 45.3 | 46.6 |
| Acetic acid (by filtration) | 47.7 | 47.1 |
| C | 19.4 | 18.9 |
| H | 2.65 | 3.1 |

- Up to 50% of the tin contained in the tin acetate product was in the stannic, $\text{Sn}(\text{IV})$, state.

Since the empirical formula is in agreement with the composition



- the tin acetate product is referred to hereinbefore as $\text{SnAc}_2 \cdot \text{H}_2\text{O}$, but the precise nature of the substance is uncertain.

EXAMPLE 95

- A selection of the polyesters from the examples described hereinbefore, both according to our invention and outside of our invention were melt-spun at a spinning temperature of 287°C. through a spinneret bearing 20 holes of 9 thousands of an inch diameter using a wind-up speed of 4,200 feet per minute to give a spun denier of 157. This yarn was drawn at 2,500 feet per minute using a draw ratio of 3.22, over a hot roll at 90°C. and a hot plate at 170°C. Examination of the result-drawn yarns showed that the improved lumin-

ance and value for luminance minor yellowness of the polyesters according to our invention were maintained in the drawn yarns.

WHAT WE CLAIM IS:—

1. A process for the preparation of a high molecular weight linear polyester by the polycondensation of a bis(ω -hydroxyalkyl) terephthalate using as polycondensation catalyst or catalysts either a compound containing pentavalent antimony and tin which is soluble in the reaction mixture or both a compound of antimony in the pentavalent state which is soluble in the reaction mixture and a compound of tin which is soluble in the reaction mixture, the quantity of antimony compound and the quantity of tin compound present being in each case sufficient to correspond to the presence of at least 5 parts per million of the metal based on the bis(ω -hydroxyalkyl) terephthalate and the quantities of antimony compound and of tin compound being such as to correspond to at least 0.5 atoms but not to exceed 30 atoms of antimony to one atom of tin.

2. A process according to Claim 1, wherein the quantities of antimony compound and of tin compound are such as to correspond to at least 1 atom but not to exceed 10 atoms of antimony to one atom of tin.
3. A process according to Claim 1 wherein the quantities of antimony compound and of tin compound are such as to correspond to at least 1.3 atoms but not to exceed 5 atoms of antimony to one atom of tin.
4. A process according to any of Claims 2 or 3 wherein the quantity of antimony compound present is such as to correspond to not more than 1,000 parts per million of antimony metal based on the bis(ω -hydroxyalkyl) terephthalate, and the quantity of tin compound present is such as to correspond to not more than 500 parts per million of tin metal based on the bis(ω -hydroxyalkyl) terephthalate.
5. A process according to any of Claims 1—4 wherein the antimony compound is antimoninic acid, antimony pentaglycoloxide, antimony pentoxide or potassium antimonate.
6. A process according to any of Claims 1—5 wherein the tin compound is stannous formate, stannous acetate, stannous octanoate, stannous oxalate, stannous chloride, stannic chloride, dioctyl thio tin, dibutyl tin oxide, dibutyl tin acetate, dibutyl tin laurate, dibutyl tin maleate or tetrabutyl tin.
7. A process according to any of Claims 1—6 wherein the polyester is a fibre-forming polyester.
8. A process according to any of Claims 1—7 wherein the polyester is a polyester of which at least 80% of its units are of a single alkylene terephthalate.
9. A process according to Claim 8 wherein the alkylene terephthalate is ethylene terephthalate.
10. A process according to any of Claims 1—7 wherein the polyester is poly(ethylene terephthalate).
11. A process for the preparation of a high molecular weight linear polyester according to Claim 1 as hereinbefore described with particular reference to the examples.
12. A high molecular weight linear polyester as prepared by the process claimed in any of Claims 1—11.
13. Fibres or filaments prepared from a polyester according to Claim 12.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.